Stable Isotope Geochemistry

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This review is intended principally to be a reasonably comprehensive bibliography. It covers papers by workers in stable isotope geochemistry in the United States that have been published or presented at national meetings since the last quadrennial report. The titles of the papers in the bibliography are in most cases indicative of the general content, so only the highlights are described below.

Reviews

A review of oxygen, carbon, and hydrogen isotope geochemistry in the marine environment was written by *Garlick* [1974]. Several reviews concerning the use of stable isotopes in studies of ore deposits and hydrothermal alteration were published in the October 1974 issue of *Economic Geology*. Sulfur and carbon isotopes were discussed by *Rye and Ohmoto* [1974], hydrogen and oxygen isotopes were discussed by *Taylor* [1974*a*], and a general review was given by *White* [1974].

Meteorites

Without question, the most exciting recent development with regard to meteorites was the discovery by *Clayton et al.* [1973] and *Clayton* [1974] of an ^{16}O-enriched component in carbonaceous chondrites. This discovery was made by carefully measuring the $^{17}O/^{16}O$ depletions in certain meteorites (notably in Allende) relative to ordinary chondrites. Instead of being half the $^{18}O/^{16}O$ depletions, as is normally the case and as is expected on the basis of chemical or physical isotopic fractionation effects, the data indicated that these carbonaceous chondrites represented a mixture of (1) a component having an $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratio similar to that of the earth, the moon, and ordinary chondrites and (2) an ^{16}O-enriched component that may be comprised of essentially pure ^{16}O; the latter component is identified as material that existed prior to condensation of the solar nebula 4.6 b.y. ago. These effects and their implications are presently under active investigation by R. N. Clayton and his associates.

Onuma et al. [1972*a*, 1973] measured $^{18}O/^{16}O$ ratios in a number of minerals from meteorites and showed that for most ordinary chondrites, equilibrium fractionations were 'frozen in' for various mineral pairs at $T > 800°C$. *Onuma et al.* [1972*b*], trying to explain the whole-rock $^{18}O/^{16}O$ variations in meteorites, proposed an oxygen isotope 'cosmothermometer.' This purported to explain these isotopic variations in terms of equilibrium crystallization at varying temperatures in the solar nebula. However, in light of the aforementioned discoveries by *Clayton et al.* [1973*a*], the cosmothermometer was shown to be invalid, and this was acknowledged by *Onuma et al.* [1974].

Deines and Wickman [1973] measured the $^{13}C/^{12}C$ ratios in various carbon compounds in iron meteorites and showed that with $\delta^{13}C \approx -7$, the 'graphitic' carbon was enriched in ^{13}C by 10–15‰ relative to the rest of the carbon in the meteorite. The $\delta^{13}C$ values are highly variable, even within a single meteorite or in a single nodule within a meteorite.

Lunar Rocks and Minerals

Stable isotope studies of returned lunar samples have served mainly to confirm that the observed isotopic effects are essentially independent of geographic location on the moon. Very similar relationships have now been observed in Apollo 11, 12, 14, 15, 16, and 17 samples and in the Luna 16 and 20 samples.

An important result is that the $^{18}O/^{16}O$ ratios of lunar igneous rocks are essentially identical to those of mafic and ultramafic igneous rocks on earth, as well as to the values in ordinary chondrites. All these rocks are distinctly enriched in ^{18}O relative to the basaltic achondrites. The $^{18}O/^{16}O$ fractionations among coexisting minerals are all indicative of very high temperatures of crystallization ($T \approx 1000°C$ or higher), very similar to values observed in fresh terrestrial basalts [*Clayton et al.*, 1971, 1972*a*, 1973*b*, *c*; *Clayton*, 1972, 1973; *Epstein and Taylor*, 1971, 1972, 1973*a*, *b*, *c*; *Taylor and Epstein*, 1973*a*, *b*].

The lunar regolith samples are all slightly enriched in $^{18}O/^{16}O$, $^{30}Si/^{28}Si$, $^{13}C/^{12}C$, and $^{34}S/^{32}S$ relative to the parent lunar igneous rocks. *Epstein and Taylor* [1971, 1972, 1973*a*, *b*, *c*] and *Taylor and Epstein* [1973*a*] showed that the oxygen and silicon isotope effects were surface-correlated and by a series of 'F_2 stripping' experiments demonstrated that portions of the amorphous coatings on the grains comprising the regolith were enriched in ^{18}O and ^{30}Si by at least +50 and +25‰, respectively. These enrichments in ^{30}Si are by far the greatest that have yet been shown to exist in nature. These isotopic effects are due to particle bombardment of the regolith with consequent volatilization and vapor fractionation. The lighter isotopic species have been preferentially lost from the moon because of the kinetics involved in the vaporization-condensation process. The above workers, together with *Kaplan and Petrowski* [1971], *Smith et al.* [1973], and *Chang et al.* [1974], have shown that for carbon there is a similar enrichment in the heavy isotope in the soils, as well as an accompanying increase in carbon content, although *Friedman et al.* [1971, 1974*b*] have questioned these generalizations regarding the analytical results. All of the above workers conclude that, except for small amounts of spallation deuterium in some samples, the hydrogen in the lunar regolith is extremely low in deuterium and is essentially a result of bombardment of the soil by solar wind protons. However, there is disagreement between *Friedman et al.* [1974*b*] and *Epstein and Taylor* [1974] on the origin of the relatively large amounts of H_2O found in lunar 'rusty' breccia 66095, as well as on the

trace amounts of water found in all other returned regolith samples. Epstein and Taylor found that this 'lunar' H_2O was essentially identical to adsorbed terrestrial meteoric water vapor in both its $^{18}O/^{16}O$ ratio and its D/H ratio, whereas Friedman et al. interpreted their own isotopic results as indicating a true lunar origin for the H_2O.

Sedimentary Rocks

Some extremely ^{18}O rich cherts from the east African saline lakes have been studied by *O'Neil and Hay* [1973]. Extensive studies of the D/H and $^{18}O/^{16}O$ ratios have been made in modern and ancient marine cherts [*Knauth and Epstein*, 1971, 1973*a*, *b*; *Knauth*, 1974; *Kolodny and Epstein*, 1974; *Mopper and Garlick*, 1971]. These have been utilized to place some constraints on and to make estimates of the isotopic variations in ocean water as a function of time as far back as the middle Precambrian. The data also suggest that it may be possible to obtain information about the temperatures of these ancient waters. Some of the above studies are in conflict with the interpretations (but not the data!) of *Perry and Tan* [1972] on early Precambrian cherts; they have suggested that ancient ocean waters were significantly depleted in ^{18}O relative to the present-day oceans.

Kastner and Lawrence [1971] have measured the $^{18}O/^{16}O$ fractionations between coexisting authigenic feldspar and carbonate, and *Henderson et al.* [1971] studied coexisting authigenic silica and montmorillonite. *Lawrence and Taylor* [1971, 1972] made extensive studies of D/H and $^{18}O/^{16}O$ in soils and showed that the isotopic variations in modern soils formed on igneous parent rocks show a marked parallelism to the variations shown by local meteoric waters, this parallelism indicating that the new clay minerals and hydroxides formed in situ in the soils typically form in approximate isotopic equilibrium with their coexisting waters. However, only minor reequilibration or isotopic exchange occurs between these waters and the relict parent minerals present in the soils (including clays). *Yeh and Savin* [1974] have studied quartz-clay ^{18}O fractionations as a function of grain size and depth in deep cores from the Gulf of Mexico region ($35°C < T < 170°C$). Isotopic disequilibrium is prevalent, except in the <0.1-μ-sized fractions, where equilibration apparently has occurred. It may be possible to apply this technique to studying temperatures of shale diagenesis. Oxygen isotopic studies of micron-sized quartz in soils from Hawaii demonstrate that this quartz ($\delta^{18}O \approx +18$) is derived from atmospheric dust and is isotopically similar to the quartz in pelagic sediments of the North Pacific Ocean. *Churchman et al.* [1973] have observed similar quartz in many shales and in Pliocene-Pleistocene offshore sediments.

Stable isotope studies of minerals associated with Precambrian iron formations in Minnesota and Australia are reported by *Perry et al.* [1973] and *Becker and Clayton* [1972]. Sedimentary carbonates and foraminifera have been investigated by *Tan and Hudson* [1971*a*, *b*], *Hecht and Savin* [1970, 1971, 1972], and *Douglas and Savin* [1971, 1973]. *Murata et al.* [1972] have examined carbonates in phosphate-rich sedimentary formations in the western United States.

Metamorphic Rocks

One of the remarkable enigmas of oxygen isotope geochemistry is the discovery of systematic ^{18}O depletions in kimberlite eclogites by *Garlick et al.* [1971*a*]. These eclogites from the Roberts Victor pipe in South Africa definitely came from deep in the mantle, and yet they are depleted in ^{18}O by as much as 3‰ relative to mantle-derived igneous rocks such as basalts and ultramafic rocks. The ^{18}O depletions are related to the chemistry and petrography of the eclogites, and *Garlick et al.* [1971*a*] interpret these systematics as possibly being a result of fractional crystallization in a mantle magma chamber; they postulate that these anomalous effects might be due to hypothetical changes in the melt crystal $^{18}O/^{16}O$ fractionations at very high pressures. However, no such pressure effects have yet been observed in any experimentally investigated systems, the most recent investigations being those of *Clayton et al.* [1972*c*].

Taylor [1970] showed that during Grenville metamorphism in the Adirondack Mountains there was a large-scale homogenization of $^{18}O/^{16}O$, the igneous rocks (notably the anorthosite massifs) becoming enriched in ^{18}O and the metasedimentary rocks (notably the carbonates) becoming depleted in ^{18}O. *Shieh and Schwarcz* [1974] have also shown that in certain areas elsewhere in the Grenville province in Canada there have apparently been large-scale changes in the whole-rock $\delta^{18}O$ values of metasedimentary paragneisses; large areas of igneous and metamorphic rocks in the Grenville province have abnormally low $\delta^{18}O$ values. All these effects seem to indicate that during metamorphism in migmatite terranes there are massive interactions between the rocks (or magmas) and very large quantities of H_2O- or CO_2-rich fluids of deep-seated origin.

Stable isotope studies of low-grade burial metamorphism are particularly suitable because the isotopic fractionations are so large at low temperatures. However, mineral separations are correspondingly much more difficult because of the fine-grained nature of the rocks. *Eslinger and Savin* [1973*a*] were able to overcome these difficulties to some extent in their studies of a 10-km-thick section of late Precambrian metasedimentary rocks in Montana. They showed that it may be possible to do oxygen isotope geothermometry on such rocks by using quartz-illite pairs; systematic reductions in both the $^{18}O/^{16}O$ fractionations and the whole-rock $\delta^{18}O$ values occur as one proceeds downward in the sedimentary section.

Igneous Rocks

The δD value of deep-seated water from the mantle has been estimated by *Sheppard and Epstein* [1970] to be about -50 ± 20‰ on the basis of phlogopites from a number of kimberlite pipes; the average phlogopite δD value is -58 ± 18. Very much lower δD values as well as anomalously low $\delta^{18}O$ values have been observed in igneous rocks from a number of areas by *Taylor* [1971, 1973, 1974*b*, *c*], *Taylor and Forester* [1971, 1973], *Forester and Taylor* [1972, 1974], *Sheppard and Taylor* [1974], and *O'Neil et al.* [1973]. In all the above areas epizonal stocks (many of them are ring dikes) have intruded volcanic ter-

ranes; it is clear that large-scale meteoric-hydrothermal convective circulation systems have been established in the vicinity of the intrusions, which act as gigantic heat engines. The $\delta^{18}O$ and δD depletions in the igneous rocks in general occurred after crystallization, as is shown, for example, by the anomalously large quartz-feldspar ^{18}O fractionations that are typically found. These isotopic effects apparently occur everywhere that an epizonal intrusion or relatively shallow batholith is emplaced into highly jointed permeable country rocks. Typically, these rocks show turbid feldspars, granophyric textures, miarolitic cavities, and chlorite-epidote-actinolite alteration assemblages. The H_2O in all these situations is essentially derived entirely from meteoric groundwaters; no isotopic traces of original magmatic water remain. Much so-called 'deuteric' alteration in igneous rocks is thus apparently caused by influx of meteoric groundwaters rather than by late-stage magmatic fluids.

An important recent development in the isotopic study of igneous rocks is the unequivocal demonstration of the existence of low-^{18}O magmas by *Forester and Taylor* [1972, 1974], *Muehlenbachs* [1973], *Muehlenbachs et al.* [1974], *Taylor* [1974*b*, *c*], *Wenner* [1973], and *Friedman et al.* [1974*c*]. These low-^{18}O magmas are typically found in regions where there are extensive areas of low-^{18}O rocks that are known to have been produced by meteoric-hydrothermal alteration. Therefore although there are a few other rock types known with $\delta^{18}O < +5.5$ (e.g., the eclogites of *Garlick et al.* [1971*a*]), it is logical to attribute the ^{18}O depletions of these magmas to some kind of interaction with low-^{18}O meteoric groundwaters at high temperatures. It is doubtful, however, that the isotopic effects can be explained simply by direct influx of H_2O into the magmas because some of the ^{18}O depletions are so large (at least 4‰). Even at saturation the magmas cannot dissolve enough low-^{18}O H_2O to produce such $\delta^{18}O$ values, so a cycling or migration of meteoric H_2O into and then out of the magma chamber would be required. It is thus probable that many low-^{18}O magmas are produced by remelting of the hydrothermally altered roof rocks above a magma chamber or by assimilating large quantities of such material in the upper portions of the magma chamber. *Friedman et al.* [1974*c*] have demonstrated very nicely that the ^{18}O depletions observed in a sequence of eruptions of rhyolitic ash flow tuff magmas change systematically with time. In a given sequence the later eruptions are lower in ^{18}O, as is expected if the upper parts of the magma chamber are being progressively depleted in ^{18}O.

All the ^{18}O-depleted igneous rocks mentioned above are Tertiary or late Mesozoic in age. In an investigation of several somewhat analogous Precambrian occurrences (the Muskox, Bushveld, Duluth-Keweenawan, and St. Francois Mountains igneous complexes) anomalously high ^{18}O igneous rocks were found instead of ^{18}O-depleted rocks [*Wenner and Taylor*, 1972; *Taylor*, 1974*c*]. The high-^{18}O effects are associated with negative quartz-feldspar ^{18}O fractionations (i.e., reversed from the normal igneous values, indicating strong disequilibrium), suggesting either interaction with unusually ^{18}O-rich hydrothermal fluids or alteration at very low temperatures ($\leq$200°C). They are also typically associated with strong discrepancies between the Rb-Sr isochron ages and the U-Pb zircon ages. The only known Precambrian occurrence that is similar to the Tertiary and Mesozoic examples is a late Precambrian (650 m.y. old) granite batholith in the Seychelles Islands [*Taylor*, 1974*b*]. Locally, meteoric-hydrothermal alteration effects are present, and a very large pluton of granitic magma on the island of Mahé was apparently intruded as a homogeneous low-^{18}O melt with $\delta^{18}O \approx +3.1$.

Stuckless and O'Neil [1973] have measured $\delta^{18}O$ values of coexisting phenocrysts and groundmass from volcanic rocks in Arizona. Similar measurements have also been made by *Anderson et al.* [1971] for a large number of volcanic rocks (mostly basalts from Hawaii); the ^{18}O fractionations are small and very uniform, indicating attainment and 'freezing in' of equilibrium at magmatic temperatures and allowing development of a semiempirical plagioclase-magnetite ^{18}O geothermometer.

Turi and Taylor [1971*a*, *b*] have studied the interactions between granitic plutons and high-^{18}O metasedimentary country rocks, showing that ^{18}O contamination effects typically extend far into the pluton, well beyond any noticeable chemical or petrographic indications of contamination. *Turi and Taylor* [1974] have studied $\delta^{18}O$ variations in the volcanoes and epizonal plutons of the Pliocene-Pleistocene Roman and Tuscan magmatic provinces in Italy. The leucite-bearing volcanic rocks of the Roman province become progressively enriched in ^{18}O as one moves north from Mount Vesuvius toward the Tuscan province. This enrichment parallels an enrichment in $^{87}Sr/^{86}Sr$ in these volcanic rocks and clearly indicates strong contamination of these mantle-derived magmas with high-^{18}O Tuscan magmas and/or sedimentary country rocks. The rhyolitic magmas of the Tuscan province are all extremely enriched in ^{18}O ($\delta \approx +12$ to $+18$) and must have been essentially wholly derived by anatectic melting of sedimentary or metasedimentary rocks.

Deines and Gold [1973] have made an extensive study of $\delta^{13}C$ values of carbonatites and kimberlites. They have shown that although there are distinct isotopic differences between different bodies, the average $\delta^{13}C$ value of deep-seated carbon is remarkably similar, whether it comes from carbonatites (-5.1 ± 1.4), kimberlite carbonates (-4.7 ± 1.2), or diamonds (-5.8 ± 1.8). *Fuex and Baker* [1973] and *Pearson and Baker* [1974] have measured carbon isotope variations in a variety of igneous rocks including some mafic and ultramafic rocks presumably derived from the mantle. The $\delta^{13}C$ of reduced carbon in these rocks is typically very low ($\delta^{13}C \approx -20$ to -27), much lower than it is in coexisting carbonate; the reasons for this are still poorly understood.

Ore Deposits

Recently there has been a remarkably rapid expansion in the number and the quality of stable isotope studies of ore deposits. Such studies probably represent the best geochemical techniques available for discerning the origin of the H_2O, CO_2, H_2S, and other volatile species involved in ore deposition. As was shown by *Ohmoto* [1972] and *Ohmoto and Shettel* [1974], these studies may also be able to provide information about such variables as f_{O_2} and *p*H. An important development has been the demonstration that heated meteoric groundwaters are a major consti-

tuent of the ore-forming fluids in many localities and are usually overwhelmingly dominant in the latest stages of mineral deposition. In particular, all epithermal Au-Ag deposits and many epithermal base metal deposits in volcanic terranes seem to have formed exclusively from meteoric-hydrothermal fluids [*Taylor*, 1973; 1974*c*; *O'Neil et al.*, 1973; *O'Neil and Silberman*, 1974; *Rye et al.*, 1974*a*; *Bethke et al.*, 1973; *Casadevall et al.*, 1974]. The ore fluids which formed the large Butte, Montana, copper deposit, wholly emplaced within a highly fractured quartz monzonite pluton inside the Boulder batholith, also were dominantly meteoric in origin [*Sheppard and Taylor*, 1974].

Sheppard et al. [1971] have identified magmatic H_2O as the dominant constituent involved in the K feldspar-biotite alteration in the core zones of porphyry copper deposits, while meteoric-hydrothermal waters were mainly responsible for the outer zones of pyrite-sericite and kaolinite-montmorillonite alteration. Similarly, two isotopically distinct waters were found to have been present during formation of the Climax porphyry molybdenum deposit [*Hall et al.*, 1974].

An important series of detailed O, H, C, and S isotope studies of minerals and fluid inclusions in individual ore deposits has been carried out by *Rye and Rye* [1974], *Rye et al.* [1974*b*], *Rye and Sawkins* [1974], *Rye and Kelly* [1974], *Pinckney and Rye* [1972], *Landis et al.* [1972], *Robinson and Ohmoto* [1973], and *Ohmoto and Rye* [1974]. In detail, each ore deposit exhibits unique characteristics, and the stable isotope studies demonstrate clearly that a wide variety of aqueous fluids are involved; generally, waters from two or more sources play a role, and the types and proportions vary from deposit to deposit. Typically, meteoric waters are involved at some stage, commonly late in the paragenesis, and in some cases there is evidence for more than one type of meteoric water. Magmatic waters, saline formation waters, and ocean waters have been identified as agents of ore deposition in individual deposits by utilizing the stable isotope variations as tracers. In most of the deposits associated directly with intrusive stocks, the carbon and sulfur appear to be of igneous derivation in spite of the complex origins of the H_2O.

At the Homestake gold mine in South Dakota, *Rye and Rye* [1974] were able to show that the important period of mineralization was of Precambrian age, not Tertiary, as had commonly been believed, by showing that the sulfur and lead in the deposit were derived from the Precambrian sedimentary formation that is the host rock for the Au-bearing quartz veins. *Mauger* [1972] showed by means of $\delta^{34}S$ analyses that the Paleozoic Ducktown, Tennessee, massive sulfide deposit was syngenetic-metamorphic in origin; this origin was also confirmed by a δD and $\delta^{18}O$ study [*Addy and Ypma*, 1973]. It thus begins to appear that the Phanerozoic massive sulfide deposits may derive their sulfur largely by reduction of seawater sulfate [e.g., *Lusk*, 1972]. However, sulfur isotope studies of Precambrian massive sulfide deposits are not so clear-cut [*Mauger*, 1973], perhaps reflecting our lack of knowledge of the $\delta^{34}S$ variations in seawater sulfate during the Precambrian. *Brown* [1973] has put together some data on this problem.

Other sulfur isotope studies of ore deposits are by *Field* [1973], *Field and Moore* [1971], *Lange and Cheney* [1971], and *Pinckney and Rafter* [1972]. *Field and Lombardi* [1972] and *Jensen et al.* [1971] have shown that $\delta^{34}S$ values can be used to distinguish between primary sulfates and supergene sulfates (e.g., alunites) in mineral deposits.

Hydrothermal Alteration and Water-Rock Interactions

Much of this material has been covered in the above sections on igneous rocks and ore deposits. However, stable isotopic studies of some modern geothermal areas have been done in Imperial Valley, California [*Coplen*, 1973, 1974], at Broadlands, New Zealand [*Eslinger and Savin*, 1973*b*], at the Geysers, California [*Lambert and Epstein*, 1974], and on a travertine-depositing hot spring [*Friedman*, 1970].

Muehlenbachs and Clayton [1971, 1972*a*, *b*] and *Muehlenbachs* [1974] have studied the oxygen isotopic effects produced by interactions between ocean water and submarine igneous rocks, principally oceanic basalts, with regard to both weathering in the presence of seawater and hydrothermal alterations involving seawater. The interactions between heated seawater and submarine basalts are a very widespread phenomenon. *Wenner and Taylor* [1973] analyzed δD and $\delta^{18}O$ values of submarine serpentinites. They showed that the oceanic serpentines are isotopically distinct from all continental (on land) serpentines and that they must be the result of interaction between heated ($T > 100°C$) ocean water and ultramafic rocks at mid-ocean ridges. These data all indicate the great importance of deep convective circulation of seawater heated by igneous intrusions at midocean ridges.

Wenner and Taylor [1974] and *Magaritz and Taylor* [1974] have made extensive studies of δD and $\delta^{18}O$ values in serpentinized ultramafic rocks. They demonstrated that antigorites typically have very uniform δD and $\delta^{18}O$ values identical to those of most metamorphic chlorites; it is thus implied that the antigorites form by reaction with metamorphic pore fluids at high temperatures, this implication being confirmed by the small values of the antigorite-magnetite ^{18}O fractionations [*Wenner and Taylor*, 1971]. The δD values of lizardite-chrysotile serpentines, on the other hand, show a strong latitudinal dependence. They become progressively depleted in deuterium (and to a lesser degree in ^{18}O) as one moves north, interactions with meteoric groundwaters thus being clearly indicated. This alteration occurs at relatively low temperatures (~100°C or less), as is shown by the very large serpentine-magnetite ^{18}O fractionations.

Hydrosphere and Atmosphere

On the basis of previous δD and $\delta^{18}O$ studies, it is known that the H_2O in essentially all hot springs and geysers in the world is of surface derivation. However, *White et al.* [1973] have recently discovered some anomalous geothermal waters in the Franciscan formation of California that have $\delta^{18}O \approx +6$ and whose δD values are significantly different from those of local meteoric waters. They interpret these waters to be true metamorphic waters that have migrated upward to the surface. *Kharaka et al.* [1973] have studied the isotopic variations of oil field brines in sedimentary rocks in California. Modifications

that take place in trapped ocean water present interstitially in deep-sea sediments are discussed by *Friedman and Hardcastle* [1973, 1974] and *Lawrence* [1973]. Similar but more complete studies of interstitial waters in coastal sediments are reported by *Nissenbaum et al.* [1972]. *Matsuo et al.* [1972] have studied δD variations in minerals of saline lakes where evaporation and enrichment in deuterium have been very strong. Comprehensive isotopic studies of groundwaters in arid regions of the western United States have been carried out by *Winograd and Friedman* [1972] and *Simpson et al.* [1970].

Kroopnick [1974], *Kroopnick and Craig* [1972], and *Kroopnick et al.* [1972] have investigated $\delta^{18}C$ and $\delta^{18}O$ variations in atmospheric oxygen and CO_2 and have studied the effects of their interactions with ocean waters. *Friedman and Scholz* [1974] have studied δD variations in atmospheric hydrogen. Atmospheric carbon monoxide has been studied by *Stevens et al.* [1972]. *Rodrigues and Epstein* [1974] showed that stable isotope variations in atmospheric CO_2 in an urban atmosphere can be used as tracers to identify CO_2 derived from natural sources, from burning liquid petroleum, and from burning natural gas.

Holland [1973] has examined the implications of $\delta^{34}S$ variations in marine sulfates for the development of atmospheric oxygen. Theoretical models of the variation in $\delta^{18}O$ in the oceans with time have also been developed, but at present they are not very satisfactory [*Chase and Perry*, 1972; *Becker et al.*, 1973].

Stable isotope studies of meteoric waters, snow, and ice can have important application to climatic problems, both in the present and in the Holocene and Pleistocene. For example, *Friedman and Smith* [1972] have examined the climatic implications of δD variations in snow in the Sierra Nevada, California; *Gow and Epstein* [1972], *Gow et al.* [1973], and *Epstein et al.* [1970] have examined δD and $\delta^{18}O$ variations in ice cores from the Antarctic ice sheet. Systematic isotopic variations occur as a function of depth to more than 2000 m at Byrd Station. These give climatic information about the last 75,000 years.

Climatic information about the older Pleistocene is obtained from $\delta^{18}O$ measurements on marine carbonates such as foraminifera in deep-sea cores [*Emiliani*, 1970, 1971; *Shackleton and Opdyke*, 1974; *Ninkovich et al.*, 1974; *Van Donk*, 1973]. A relatively complete Pleistocene record has now been obtained. These techniques can also be extended back as far as the Cretaceous, although with a lesser degree of certainty [*Douglas and Savin*, 1971, 1973]. With certain reservations, similar techniques can also be applied to freshwater carbonates [*Stuiver*, 1970].

Organic Geochemistry

Oehler et al. [1972] have shown that the reduced carbon in early Precambrian cherts of the Fig Tree and Onverwacht groups in South Africa is isotopically similar (average $\delta^{13}C_{PDB} = -28.7$) to photosynthetically produced organic matter of younger geologic age. This similarity suggests the existence of autotrophic organisms as far back as 3.3×10^9 years ago. However, reduced carbon in the lowermost Onverwacht cherts is anomalously heavy ($\delta^{13}C \approx -16.5$); this discontinuity may indicate a major event in biological evolution, perhaps the time of origin of biochemical mechanisms that fractionate carbon isotopes in the modern manner. *Epstein* [1970] has reviewed other aspects of the $\delta^{13}C$ variations in Precambrian reduced carbon.

Smith and Epstein [1971] have measured $\delta^{13}C$ values in a wide variety of modern plants. They have shown that because of variations in the photosynthetic fractionation mechanisms, the higher plants fall into two categories: those with low $\delta^{13}C$ (−24 to −34) and those with high $\delta^{13}C$ (−6 to −19). The high ^{13}C group is composed of the aquatics, desert and salt marsh plants, and tropical grasses, while the low ^{13}C group comprises the rest of the plant kingdom, except for the more primitive algae, which represent a separate group with $\delta^{13}C = -12$ to −23. *Jacobson et al.* [1970*a*, *b*] have made detailed investigations of the $\delta^{13}C$ effects accompanying biological processes in plants. *Smith and Epstein* [1970] have studied $\delta^{13}C$ and δD variations in plants in a salt marsh and observed D/H fractionations of more than 50‰ between plants and H_2O, independent of the type of plant. *McCready et al.* [1974] carried out an experimental investigation of the fractionation of sulfur isotopes by yeast. *Gleason and Friedman* [1970] studied the rate at which natural D/H variations were produced in rats when their diets were transferred to food and water having a different D/H ratio.

Carbon isotope fractionations in blue green algae have been studied by *Behrens and Frishman* [1971] and *Calder and Parker* [1973]. The $^{13}C/^{12}C$ variations in organic carbon in cores of Quaternary sediments from the Gulf of Mexico have been examined by *Newman et al.* [1973]; changes in $\delta^{13}C$ of as much as 6‰ were measured across the Pleistocene-Holocene boundary. The major cause of these variations is the relative amount of terrestrial material present in the sediment. Other studies of organic matter in sediments are by *Gormly and Sackett* [1974], *Gearing and Parker* [1973], and *Sackett et al.* [1974].

Experimental Studies and Analytical Techniques

Clayton et al. [1972*b*] measured the equilibrium oxygen isotope fractionation factor for quartz-H_2O from 195° to 750°C. There are many experimental difficulties in studying this system because quartz is very resistant to hydrothermal exchange, and two different sets of results were obtained, one from 'equilibrium' runs and the other from extrapolations of 'partial exchange' runs. The reasons for these differences are poorly understood, and thus there are problems in utilizing these data in geothermometry. *Clayton et al.* [1972*c*] measured the calcite-H_2O $^{18}O/^{16}O$ equilibrium fractionation factor to pressures as high as 20 kbar and demonstrated that there is no pressure effect whatsoever. Rates of isotopic exchange are vastly increased at these high pressures, however. *Muehlenbachs and Kushiro* [1974] have measured oxygen isotope fractionations between silicate melts and CO_2. *Truesdell* [1974] has measured the effects of dissolved salts on the oxygen isotopic properties of water at high temperatures. Contrary to the situation at 25°C, where addition of NaCl to aqueous solutions has no effect on mineral-H_2O fractionations, complex effects larger than 1‰ were found at high temperatures. This has important implications both in the measurement of experimental fractionation factors carried out with salt solutions and in the calculation of the $\delta^{18}O$ of H_2O that coexisted with

natural mineral assemblages formed from saline fluids. Hydrogen isotope fractionations between H_2O and muscovite, biotite, and hornblende were studied by *Suzuoki and Epstein* [1974] at temperatures of 400°–800°C. They showed that the most important variable in controlling D/H fractionations in silicate-H_2O systems is the Mg/Fe and Al/Fe ratios of the minerals. The Mg- and Al-rich minerals concentrate deuterium relative to Fe-rich minerals. At temperatures above 450°C, however, the D/H fractionations for all these mineral-H_2O pairs plot as parallel lines on a plot of 1000 ln α versus $1/T^2$. It is thus implied that at such temperatures the D/H fractionations among minerals are not temperature-sensitive and therefore cannot be used as geothermometers. *Coplen and Hanshaw* [1973] measured the D/H and $^{18}O/^{16}O$ fractionation effects that occur during ultrafiltration of water through clay membranes. *Stewart* [1974*a*] and *Stewart and Friedman* [1973] have measured the D/H fractionations between mirabolite and ice and between aqueous salt solutions and water vapor.

Czamanske and Rye [1974] and *Salomons* [1971] measured $\delta^{34}S$ fractionations between sphalerite and galena and between galena, pyrite, and sulfur. *Hamza and Broecker* [1974] have measured the surface effects on the $^{18}O/^{16}O$ and $^{13}C/^{12}C$ fractionations between calcite, dolomite, witherite, and CO_2 at 200°C; they obtained fractionations of several per mil between the surface carbonate and the bulk carbonate, and they were also able to make estimates of the equilibrium fractionation between these carbonates and CO_2.

Several papers on isotopic standards and modifications of analytical techniques have been published by *Coplen and Clayton* [1973], *Friedman and Gleason* [1973], *Jackson et al.* [1973], and *Puchelt et al.* [1971].

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Mineralogy, Petrology, and Geochemistry of the Lunar Samples

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The years 1971–1974 mark the maturing of lunar mineralogy, petrology, and geochemistry into a full-fledged science. During these years the prime objective of lunar sample investigation teams changed from general surveys of the nature of returned lunar material into problem-oriented studies. Four general areas of interest that evolved during these years are (1) the geochemistry of the bulk moon, (2) the lunar regolith, (3) the lunar mare basins, and (4) the lunar highlands and crust. About 1000 scientists have been engaged in attempting to determine the origin and evolution of the moon. Although little new light has been shed on the ultimate problem of the origin of the moon, the following paragraphs show that the years 1971–1974 have greatly added to our understanding of the moon as an evolving planet.

About 385 kg of lunar material was returned to earth by Apollo missions 11, 12, 14, 15, 16, and 17. All of this material, plus 3 g from each of the Soviet missions Luna 16 and 20, is being studied by United States lunar scientists using a wide range of techniques and instruments. The electron microprobe, scanning electron microscope, solid state detector with multichannel analyzer, and mass spectrometer are routinely used as petrologic tools, and new instruments such as the ion microprobe mass analyzer are being developed. In addition, the small amounts of lunar samples available for a given project have prompted investigators to refine their techniques, so that routine measurements can be made on smaller and smaller samples. Rare earth element abundance patterns are now routinely determined on 1-mg fragments, and not too far in the future an isotopic age will surely be performed on an equivalent sized fragment.

The bibliography of lunar sample studies contains over 4700 citations for the years 1971–1974. About one fourth of them are contained in the proceedings of the Second, Third, Fourth, and Fifth Lunar Science Conferences, and another fourth are extended abstracts (generally 3 pages each) published by the Lunar Science Institute, Houston, Texas. These later volumes are entitled *Lunar Science III, IV, V,* and *VI* and *The Apollo 15 Lunar Samples.* The entire bibliography is available from the author in microfilm form. The bibliography at the end of this section contains only those papers cited in the text. The references are not inclusive, since many of the data and conclusions were independently obtained by several investigation teams over the span of several papers. Hence the references are meant to indicate a good starting point for further reading.

Geochemistry of the Bulk Moon

A large-scale chemical view of the lunar surface has been achieved by a remarkable series of three remote sensing experiments.

An X ray fluorescence experiment that used the sun as a source of primary X rays and recorded secondary X rays generated by the upper micron of the lunar surface was operated from lunar orbit during Apollo 15 and 16. Using